

Characteristic Behaviour of Carbon Steel Exposed to Na_2CO_3 , and NaCl Solutions of Different Concentrations.

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Abstract:-The goals of this study were to assess the influence of different salt concentrations on the corrosion resistance of carbon steel. API 5L X42 steel coupons were totally immersed in sodium chloride (NaCl) and sodium carbonate (Na_2CO_3) environments maintained at different concentrations. The weight loss technique was used in which sample coupons with known weight were totally immersed in a non flowing media of NaCl and Na_2CO_3 for a total exposure time of 1008 hours. Experimental results showed that 1.0M solution medium of Na_2CO_3 had the highest corrosion effect on carbon steel, which was mainly a function of its higher concentration based on the fact that no film was formed on the coupon. This was closely followed by the medium containing 0.5M solution of NaCl. Conclusively it was proven that the lower the concentration in media capable of forming oxide film round the coupon like in NaCl media, the higher the corrosion rate. While for environments which do not aid in film formation such as Na_2CO_3 , the higher the concentration, the higher the corrosion rate. As such carbon steels would fail fastest in an environment where the concentration of Na_2CO_3 solution is high.

Keywords: - Corrosion, Coupon, Immersion, Environment, API 5L X42 carbon steel.

I. INTRODUCTION

Oil and gas pipelines are usually made of steel. By natural process, all materials tend towards achieving a state of equilibrium, which is going back to its origin. Steel being an alloy and a material obeys this call of nature and as such must go back to its equilibrium and stable form. Hence all metals and materials must corrode. The word corrosion was derived from the Latin *corrosus* which means eaten away or consumed by degrees; an unpleasant word for an unpleasant process [1]. As such, when corrosion is being discussed, it is important to think of a combination of a material and an environment. The corrosion behaviour of a material cannot be described unless the environment in which the material is to be exposed is appropriately identified. Similarly, the corrosivity or aggressiveness of an environment cannot be described unless the material that is to be exposed to that environment is also identified. Since corrosion can never be eliminated, instead by all human effort can only be controlled or managed. This makes corrosion of steel buried underground a topical issue confronting the oil and gas industry world over. A vast majority of transmission pipelines in practice are usually protected before laying them underground using coal tar coupled with an efficient cathodic protection system, which solely aims at protecting the pipe from corrosion.

Cathodic protection is usually used in addition to coating to prevent external corrosion of pipelines while inhibitors and improved production techniques are used to minimize internal corrosion of oil and gas pipelines. This work specifically investigates the corrosion rates of API 5L X42 carbon steel in NaCl and Na_2CO_3 environments maintained at different concentrations with a view to determining the most aggressive environment that should be avoided or deserved highly protected pipeline.

These simulated soil solutions could in most cases either act as an inhibitor or a corrosion enhancer.

II. LITERATURE SURVEY

A research to investigate the effect of a high salt concentration on corrosion from low partial pressures of hydrogen sulfide (H_2S) has been conducted [2]. The main objective was to study if the high concentration of chloride could initiate localized attack in this type of H_2S system.

Also the sole purpose of Andi and others (2012) [3] in their research was to investigate the corrosion rate of carbon steel as flow line and pipeline in natural gas production with CO_2 content. The influence of variety of conditions that represent the actual conditions in practice such as CO_2 partial pressure and solution composition, particularly NaCl percentage were performed. In it, Corrosion rate of API 5L X-52 steel was examined under NaCl solution with two different environmental conditions. First condition was aerated environment and the other was in ambient CO_2 -saturated aqueous environments.

Corrosion behavior of mild steel in seawater from different sites was investigated by using weight loss method and potentiodynamic polarization test [4].

Zenati and others (2014) [5] investigated the corrosion behaviour of C-Mn steel type API 5L X60 in simulated soil solution environment and inhibitive effect, where the criterion for studying the steel aggressiveness was principally the chloride, sulphate and bicarbonate contents.

The corrosion resistance of 18-8 stainless steel in cassava fluids containing principally of hydrogen cyanide was studied [6]. The work simulated the effect of continuous use of this material in a cyanide environment where corrosion products were left. Also corrosion behaviour of nickel and stainless steel alloys in machinery and 50 Mol/L lithium hydroxide solutions under a hydrogen atmosphere at 95°C [7]. The objective of carrying out an intensive study on the corrosion resistance of medium carbon steel (MCS) and KS7 stainless steel in selected acid media was for comparison purposes [8]. The coupons were exposed to 0.5M of H₂SO₄, HCl and HNO₃ environment for 36days.

Harish and Vikas (2013) equally carried out a research on the corrosion characteristics of mild steel under different atmospheric conditions by vapour phase corrosion inhibitors. The four corrosion inhibitors N-N-Dimethylaniline (DMA), Morpholine, cyclohexyl amine and Hexamethylene imine were tested for mildsteel under different corrosive atmospheric conditions at 40°C by weight loss, Eschke test, salt spray and SEM techniques. All the four VPCIs showed very high corrosion inhibition efficiency of about 96.98%.

Wang and others (2012) however studied the corrosion behaviour of carbon steel and aluminium alloy in hydrochloric acid and sulphuric acid solutions using microwave (MW) heating and conventional bath heating method respectively. The effect of microwave heating on corrosion time was investigated using the weight loss method while the surface morphology of metals were studied alongside using the scanning electron microscope. The conclusion that MW heating was a good method of accelerating corrosion process was obtained based on the test results and surface morphology. According to their report, both the mass loss of the metals and the pH of the solutions increased with the microwave power increasing and the immersion time prolonged. However the mass loss of the specimens heated by microwave was notably higher than that heated by water bath under the same corrosion time and temperature.

Eseonu (2008) [11] used the weight loss technique in analyzing the efficiency of corrosion inhibitors on cathodic protection system has also been carried out. He immersed medium carbon steel coupons in different solutions of potassium dichromate, sodium nitrate, EC1021A, Savor CK368 and Kurizet S636. In his report, he asserted that after 2016 hours of total immersion the inhibitor EC1021A had the best inhibitive efficiency compared to the rest three.

Badmos and Ajimotokan (2009) [12] carried out an investigative research on the corrosion effect of orange fruit juice on carbon steel. Weight loss technique was used in which test coupons with known weights were immersed in the test media which were natural juice, orange juice with preservative and water for a total exposure time of 10days.

The corrosion inhibition of mild steel in sulphuric acid by methionine (MTI) has been addressed using electrochemical techniques [13]. The authors were able to study the effect of KI additives on corrosion inhibition efficiency. The results obtained showed that MTI inhibited the corrosion reaction by adsorption onto the metal/solution interface. An increase in inhibition efficiency was observed with increase in MTI concentration and synergistically increased in the presence of KI, with an optimum [KI]/[MTI] ratio 5/5, due to stabilization of adsorbed MTI cations by means of AFM surface morphological images.

Dai and others (2009) in their research paper focussed on the effect of copper in the enhancement of corrosion resistance of Cr-Mn stainless steel in 3.5% NaCl. The major objective of the author was to improve the corrosion resistance of Cr-Mn steel by alloy optimization methods characterization techniques such as Scanning Electron Microscopy (SEM), and Energy Disperse Spectroscopy (EDS) were employed to analyse the interface and phase composition of samples.

III. MATERIALS AND METHOD

In this chapter, the focus includes methods and techniques adopted as well as the materials used for this study. This contains material used, working samples adopted and relevant carbon test carried out.

3.1 Description

This study employed a quantitative analysis method to determining the corrosion rate based on weight loss method. It involved exposing the sample coupons by total immersion into the simulated solution of different concentration and measuring the loss of weight of the material as a function of time. The measurements of the specimens are taken during exposure and after removal according to ASTM G162-99(American Standard of Material and Testing, 2000a).

Experimental materials used

- Coupons made of mild carbon steel(API 5L X42)
- Solution of different concentrations
- Digital weighing balance
- Plastic brush
- Plastic containers
- Acetone(degreasing agent)
- Beaker
- 250 Cm³ volumetric flask
- Stirrer
- Na₂CO₃ salt
- NaCl salt
- Distilled water

3.2 Experimental Plan

The research duration lasted for 42days (1008 hours). At this stage, simulated laboratory work was carried out to measure the metal loss rate due to corrosion when steel coupons are exposed to various concentrations of the soil simulations. The solutions and coupon were placed into a plastic container, washed, dried and reweighed on an electronic weighing balance. Coupon retrieval was carried out periodically every seven days. As such, in order to get a time-function data of metal loss, every single sample is assumed uniform in terms of strength, thickness and corrosion resistance. Hence, metal loss measurements from respective retrieval at different time within 42 days period are considered correlated with each other.

3.3 Experimental procedure

The experimental procedure adopted was the total immersion test method in a non-flowing system because of the good reproducibility of results [11]. The experiment was simulated in a laboratory using the Choba environment, with five containers. Four of which contained solutions of NaCl and Na₂CO₃ in 0.5M and 1.0M concentrations respectively, while the fifth contained just distilled water as the control sample. Before immersing the coupons in the different solutions, the following steps were adopted.

Cleaning of corrosion coupon was as follows:

- a) The coupons were cleaned by firstly dipping coupon in distilled water for 5 minutes.
 - b) Followed by washing all the coupons in ordinary fresh water with a soft brush.
 - c) After which, the coupons were soaked in Acetone for 5 min.
 - d) Then allowed to dry in sun, followed by obtaining the initial weight (W₁) of the individual coupons using a digital weighing balance.
 - e) The sizes of the coupons measured to ascertain the area of the coupons
 - f) The weighed coupons were thereafter put back inside the solutions.
2. After every 7days (168 hours) of immersion, each of the coupons were brought out and thoroughly cleaned by same procedure as above and weighed again. Final weight is (W₂).
 3. The weight loss (W_f) in milligram and the corrosion rate was calculated using the formula below:

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times \text{Weight loss}}{\text{Area} \times \text{time} \times \text{Density}} \dots \dots (1)$$

Where:

W = weight loss in milligrams

A= area of coupon in cm²

T = time of exposure of coupon in hours

ρ = metal density in g/cm³

While the surface area of each coupon was calculated using:

$$\text{Surface Area}(A) = 2 \times [(L \times B) + (B \times T) + (L \times T)] \dots \dots \dots (2)$$

Where,

L = Length of the coupon.

B = Width of the coupon.
T = Thickness of the coupon.
D = Diameter of hole in coupon

3.3.1 Preparation of specimen

The API 5L X42 steel pipe segment used for this research work was obtained from Pipeline and Product Marketing Company (PPMC) Port Harcourt, Nigeria. The reagents used for Corrosion test included NaCl and Na₂CO₃. Concentrations 0.5M and 1.0M of these reagents were prepared and used as “soil simulation” environment.

The steel pipe segment was sectioned (cut) into coupons using a hacksaw. The cutting process was chosen so as not to alter the microstructure of the sample. A sample was subjected to chemical analysis using the metal analyzer. This was done by exposing the well-polished surface of the sample to light emission from the spectrometer. The elements contained and their proportions in the sample were revealed on the digital processor attached to the spectrometer. The results as shown in Table 1 below

Table 1 Chemical composition of API 5L X42 carbon steel (wt%)

C	Mn	P	S	Si
0.234	1.28	0.028	0.0215	0.437

Corrosion Tests

Preparation of Corroding Media

Three types of corroding media were used, namely

1. 250ml of distilled water.
2. 0.5M Na₂CO₃ solution – 13.25g of Na₂CO₃ pellets in a dry paper is weighed on a digital electronic scale. Then transferred to a clean beaker which contained some quantity of distilled water, enough to dissolve the solid Na₂CO₃ salt. The solution after vigorous shaking is transferred from beaker into a 250 cm³ volume flask. Distilled water was gradually poured into the flask until it reached the meniscus level.
3. 1.0M Na₂CO₃ solution – 26.5g of Na₂CO₃ pellets in a dry paper is weighed on a digital electronic scale. Then transferred to a clean beaker which contained some quantity of distilled water, enough to dissolve the solid Na₂CO₃ salt. The solution after vigorous shaking is transferred from beaker into a 250 cm³ volume flask. Distilled water was gradually poured into the flask until it reached the meniscus level.
4. 0.5M NaCl solution – 7.313g of NaCl pellets in a dry paper is weighed on a digital electronic scale. Then transferred to a clean beaker which contained some quantity of distilled water, enough to dissolve the solid NaCl salt. The solution after vigorous shaking is transferred from beaker into a 250 cm³ volume flask. Distilled water was gradually poured into the flask until it reached the meniscus level.
5. 1.0M NaCl solution – 14.625g of NaCl pellets in a dry paper is weighed on a digital electronic scale. Then transferred to a clean beaker which contained some quantity of distilled water, enough to dissolve the solid NaCl salt. The solution after vigorous shaking is transferred from beaker into a 250 cm³ volume flask. Distilled water was gradually poured into the flask until it reached the meniscus level.

Laboratory immersion experiment



Fig. 1: Preparation of solution media



Fig. 2: Immersion of coupons and setup



Fig. 3: Corrosion product formed on coupon

The coupons were immersed in the three solutions with concentrations as shown in the table below

Table 2 Chemical concentration of media (M)

NaCl	Na ₂ CO ₃
0.5M	0.5M
1.0M	1.0M

Every seven days (168 hrs), the coupons were brought out, washed, degreased, dried and then weighed.

Corrosion of Samples

Seven plastic bowls were provided for seven coupons of API 5L X42 carbon steel sample. Specimens were weighed with an electronic weighing balance, and the exposed surface area calculated. The samples were arranged and tagged before wholly immersing then in the respective media. The coupons were brought out every 168 hours, washed, degreased and dried before weighing them to obtain final weights so as to determine the loss in weight.

Determination of Weight Loss

No corrosion of sample was noticed the first day, however corrosion was actually noticed on the seventh day and care was taken to remove only the corrosion products using a soft plastic brush. After washing and degreasing the samples were dried and weighed with an electronic weighing balance to determine their new weights. The weight loss of each of the samples was determined and recorded. The process of washing, drying, weighing, determination of weight loss and recording was repeated consistently every 168 hours for a period of 1008 hours.

IV. RESULT AND DISCUSSION

In quantitative experimental investigations such as this, the results depend to a large extent on the way in which the data is collected. The corrosion rates of the different coupons in different solutions were calculated using the weight loss method as stated above. At the end of 1008 hours which was the duration of the research, the following were observed.

Na_2CO_3 solution of 0.5M and 1.0M concentration.

For the complete duration of 1008 hours, it was observed that both solutions of Na_2CO_3 were clear with the immersed coupons being filmless and shiny clean.

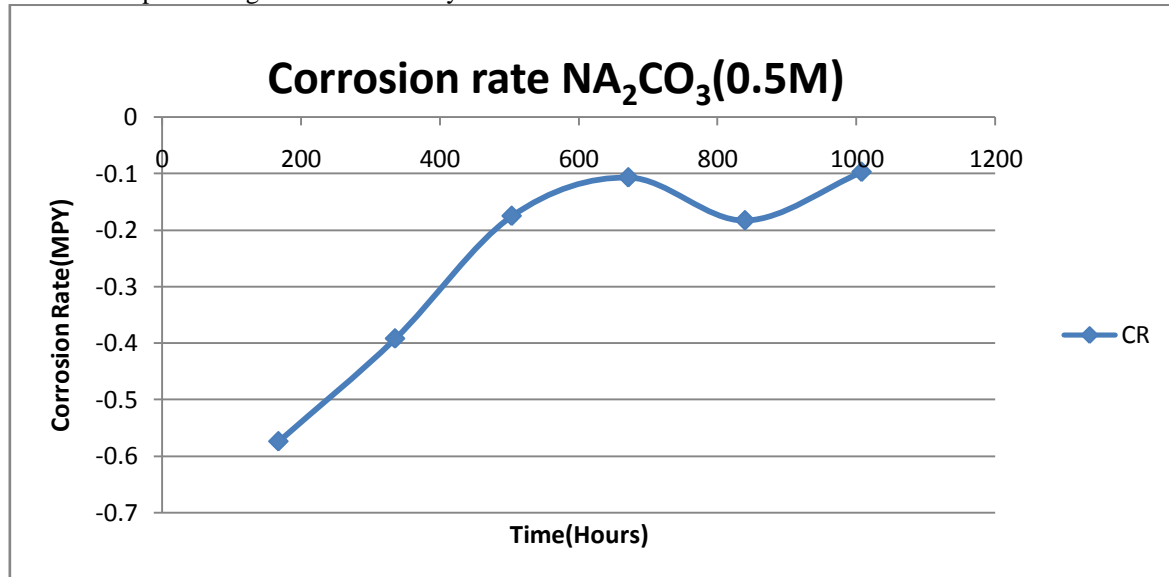


Fig. 4: Corrosion rate of coupon in 0.5M solution of Na_2CO_3

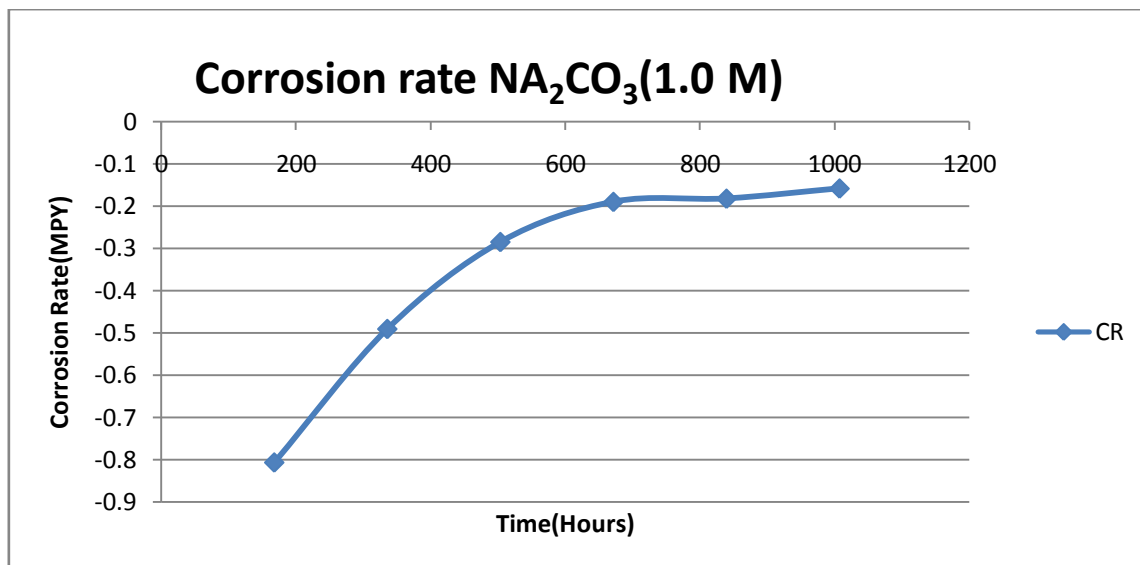


Fig. 5: Corrosion rate of coupon in 1.0M solution of Na_2CO_3

NaCl solution of 0.5M and 1.0M concentration.

After 168 hours of immersion in solution of NaCl for both solutions, it was observed that a black oxide film was formed on the surface of the coupon. The both solutions had brownish suspension (particles) in them. It was suspected that the protective film formed could possibly isolate the coupon from its environment as such visible Iron chloride film on the steel coupon was present.



Fig. 6: Brownish suspension in NaCl solution of 0.5M and 1.0M concentration

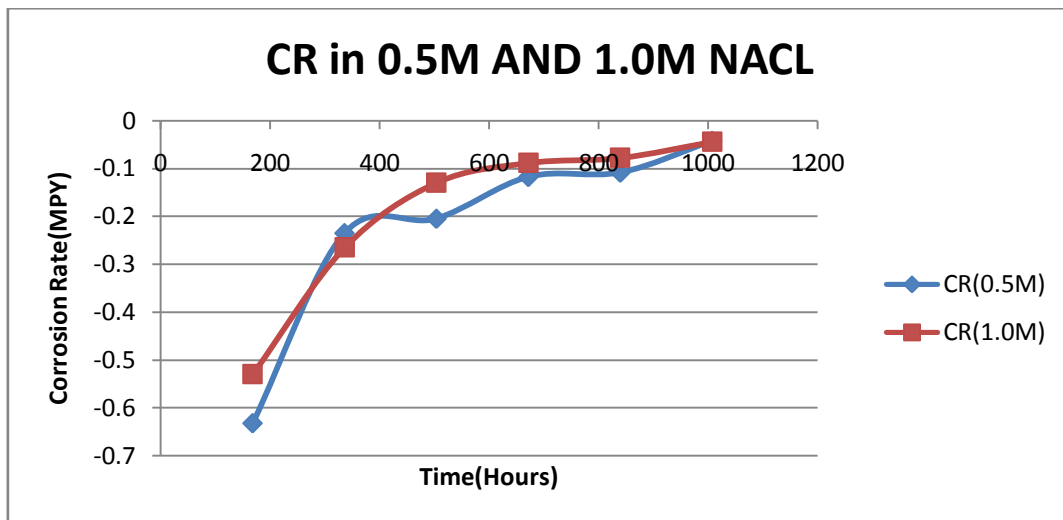


Fig. 7: Corrosion rate of coupons immersed in NaCl solution of 0.5M and 1.0M concentration

Na_2CO_3 solution of 0.5M and 1.0M concentration.

Na_2CO_3 solutions remained crystal clear for the period of experimentation as no film was visibly noticed.

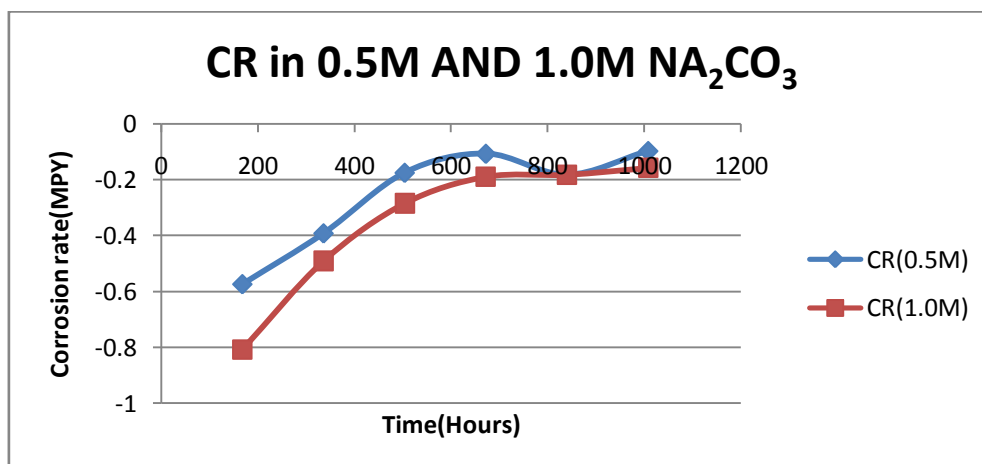


Fig. 8: Corrosion rate in Na_2CO_3 0.5M and 1.0M concentration

Corrosion behaviour in distilled water.

After 72 hours of immersion in water, it was observed a thin black film oxide round the coupon. The water solution turned brownish rust-red solution with noticeable black thin film oxide on the surface of the coupon.

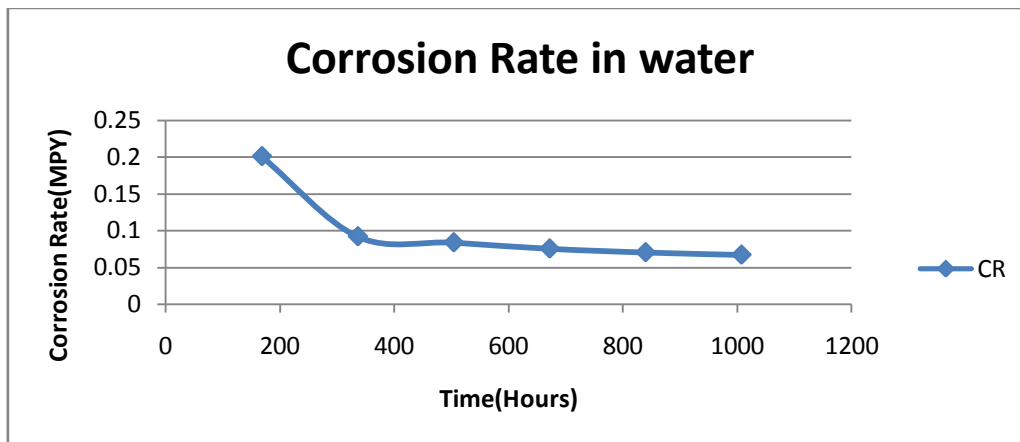


Fig. 9: Corrosion rate in distilled water

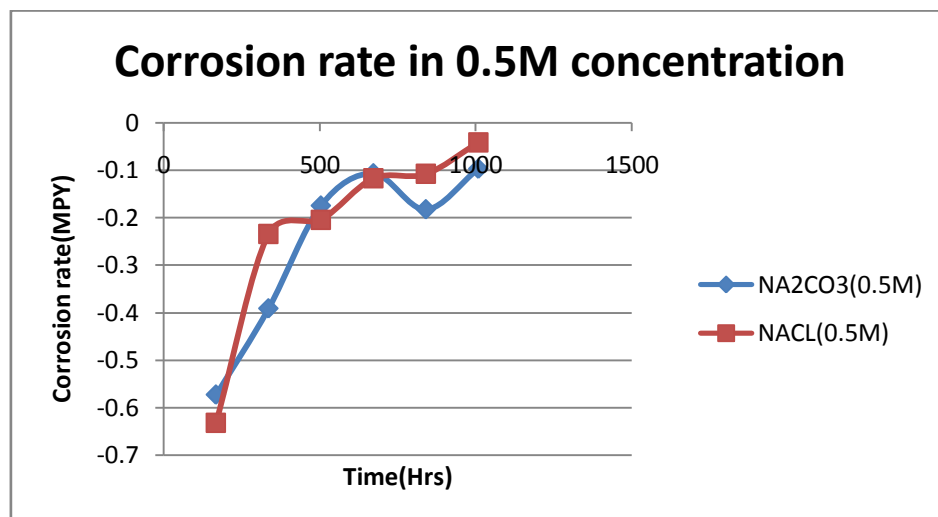


Fig. 10: Corrosion rate in Na_2CO_3 and NaCl 0.5M concentration

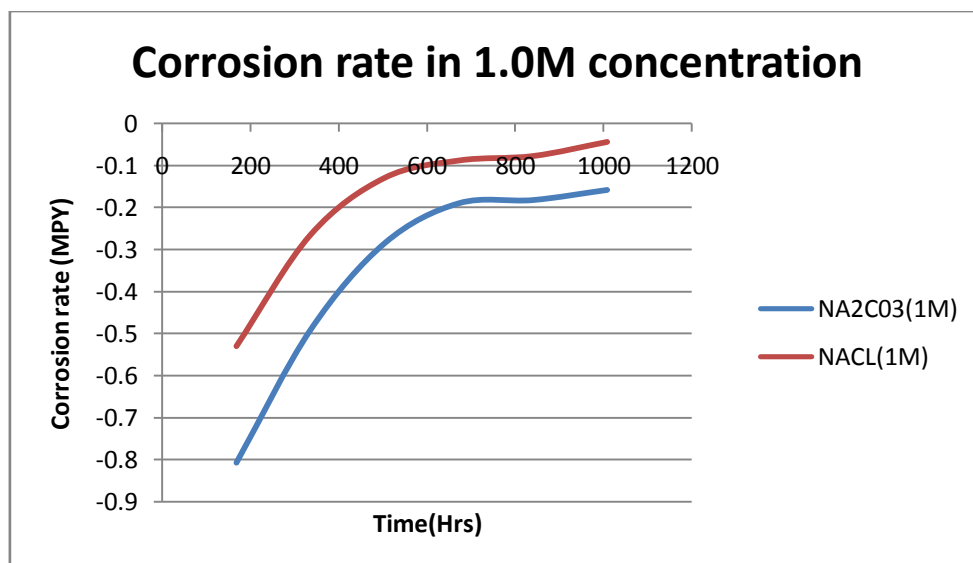


Fig. 11: Corrosion rate in Na_2CO_3 and NaCl 1.0M concentration

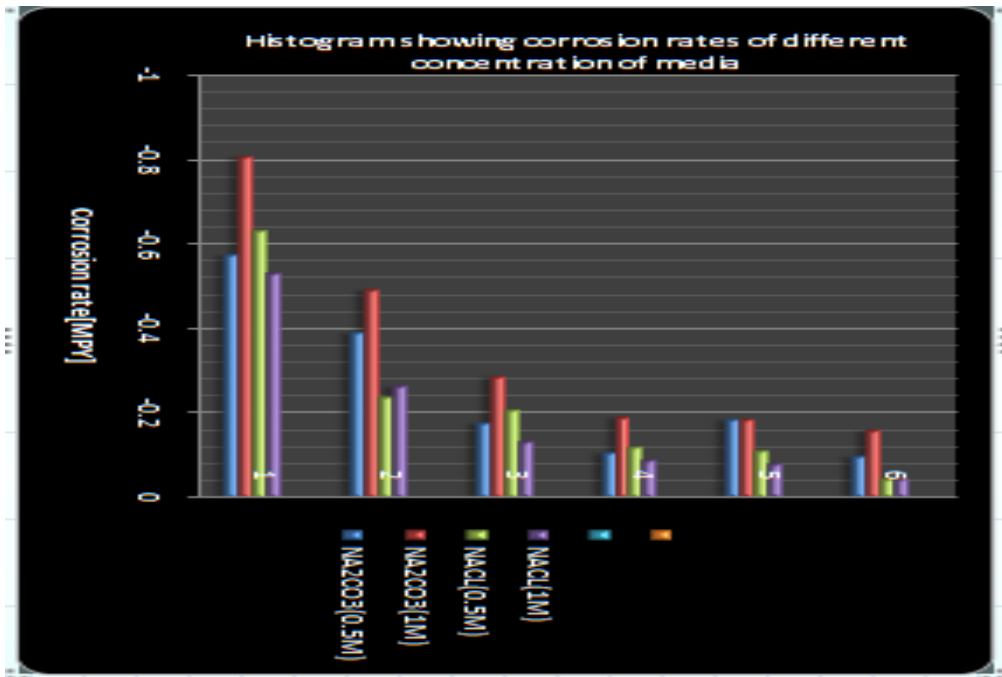


Fig. 12: Histogram showing Corrosion rate of different media of different concentration

TABLE 3: Corrosion rate of coupons in different media

T	NA ₂ CO ₃ (0.5M)	NA ₂ CO ₃ (1M)	NAOL(0.5M)	NAOL(1M)	H ₂ O
168	-0.57357	-0.80647	-0.63232	-0.52987	0.201212
336	-0.39178	-0.49053	-0.23486	-0.26493	0.092054
504	-0.17499	-0.28464	-0.20475	-0.12952	0.083838
672	-0.10694	-0.18976	-0.11743	-0.08831	0.075454
840	-0.18276	-0.18217	-0.1084	-0.07771	0.070424
1008	-0.09721	-0.15813	-0.04215	-0.04416	0.067071

TABLE 4: Weight loss in different media

TIME	WEIGHT LOSS				
	NA ₂ CO ₃ (0.5M)	NA ₂ CO ₃ (1.0M)	NAOL(0.5M)	NAOL(1.0M)	H ₂ O
168	-0.295	-0.425	-0.35	-0.3	0.2
336	-0.403	-0.517	-0.26	-0.3	0.183
504	-0.27	-0.45	-0.34	-0.22	0.25
672	-0.22	-0.4	-0.26	-0.2	0.3
840	-0.47	-0.48	-0.3	-0.22	0.35
1008	-0.3	-0.5	-0.14	-0.15	0.4

TABLE 5: Corrosion rate of coupon in both 0.5M and 1.0M Na₂CO₃

T	CR(0.5M)	CR(1.0M)
168	-0.57357	-0.80647
336	-0.39178	-0.49053
504	-0.17499	-0.28464
672	-0.10694	-0.18976
840	-0.18276	-0.18217
1008	-0.09721	-0.15813

TABLE 6: Corrosion rate of coupon in both 0.5M and 1.0M NaCl

T	CR(0.5M)	CR(1.0M)
168	-0.63232	-0.52987
336	-0.23486	-0.26493
504	-0.20475	-0.12952
672	-0.11743	-0.08831
840	-0.1084	-0.07771
1008	-0.04215	-0.04416

V. OBSERVATIONS

After the 72hours, the coupon immersed in distilled water was totally enveloped with a thin black film oxide and heavy presence of brownish rust red which coloured the water. As hours went by, the deposits turned brown identified to be ferric hydroxide. When washed, the coupon gradually turned somehow black with an appreciable loss of weight after 168 hours.

For coupons immersed in NaCl solution; after 168 hours of immersion in solution of NaCl for both solutions, when weighed an increase in weight was observed instead of a weight loss. Consequently it was also noticed a visibly black oxide film which was formed on the surface of the coupons. The both solutions had brownish suspension (particles) in them. 1.0M solution of NaCl turned brownish 336 hours while 0.5M solution turned blackish. And both coupons were turned into dull dark colour after washing and drying. This was however followed by a gradual but fluctuating decrease in weight.

Coupons immersed for the complete duration of 1008 hours in both solutions of Na₂CO₃ remained clear and the coupons upon being washed still remained clean. When weighed however it was noticed that there was weight gain rather than weight loss after the first 168 hours. Afterwards the coupon started reducing very slowly in weight.

Analysis of Result

Based on the results deduced from the table and graphs, the analysis of result shows that on the whole, the coupon immersed in distilled water had the highest while in terms of salt solutions; 1.0M of Na₂CO₃ had the highest corrosion rate followed closely by 0.5M of NaCl solution. This could be seen in the graphs shown above and based on the statistical analysis of the data.

Corrosion in distilled water seemed the least although from the outset (i.e. 168 hours), there was recorded a remarkable weight loss but the corrosion rate with time depreciated as shown in the graph.

In the case of sodium carbonate solution, 1.0M concentration seemed to be most destructive compared to the other salt solutions. Due to the filmless nature of the coupon, corrosion reaction or effect was felt most by coupon in the solution thereby leading to an accelerated corrosion rate. Since there was no film to breakdown in the first instance.

0.5M and 1.0M concentration of NaCl solution were the second and third most corrosive media respectively. As such steel immersed in solution with low chloride content most likely would be most disastrous when compared to a higher concentration of it. Seemingly the higher the concentration, the more the film build up and the lesser the corrosion reaction.

VI. CONCLUSION

Summarily it can be concluded that, the rate of corrosion of carbon steel (API 5L X42) is dependent on both the concentration of media (environmental conditions) and chemical properties of the steel. Within the limits of experimental error, conclusions drawn based on observations and result of the research are:

1. In corroding media like used in this research, corrosion of carbon steel depends on the amount of oxygen dissolved in the media and concentration of the media. The higher the concentration, the more film build up and the lesser the corrosion rate. While the smaller the concentration the higher the corrosion rate especially in NaCl solution where there was visible film formation.
2. In all the four salt media tested, 1.0M of Na₂CO₃ solution had the highest corrosive tendency, followed by 0.5M NaCl, 1.0M NaCl and the least was in 0.5M Na₂CO₃ solution.

Suggestions for Future Work

- A better and modern method of checking corrosion rate asides weight loss method should be employed in future investigations.

- It is suggested that future researchers should try developing a model to better interpret the effect of concentration increase to carbon steel.
- Future researchers are also encouraged to use the existing data in developing a model capable of predicting time of failure of carbon steels found in environments as investigated.

Limitations of Experimental Results

The possible sources of errors are likely to be from:

- 1) The instrument used: such errors include errors due to low sensitivity of instruments especially the digital weighing scale etc.
- 2) It's possible that due to the mechanical method chosen in cleaning the coupon of corrosion products, errors may be introduced, since the corrosion product may not be properly and entirely removed.

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